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DEMINERALIZATION OF WASTEWATER BY ELECTRODIALYSIS

Harold H. Takenaka, et al

Los Angeles County Sanitation District

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Slime formation (organic fouling) on the membranes and spacers of the electrodialysis stack during continuous operation significantly decreased the effectiveness of the electrodialysis process to demineralize municipal wastewater. If the total COD of the feedwater was maintained at or below 10 mg/l, a weekly enzyme-detergent flush maintained the total dissolved solids (TDS) removal in the design range of 30-35 percent.

A cost estimate for a 10 MGD single stage electrodialysis plant based on the operating results obtained at Pomona was made. The estimated cost of 19.4¢ per 1,000 gallons was based on the use of carbon-treated secondary effluent with an average TDS concentration of 540 mg/l and a total COD of 10 mg/l or less to produce a product water with 30-35 percent reduction in TDS.

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DEMINERALIZATION OF WASTEWATER BY ELECTRODIALYSIS

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise, and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The Municipal Environmental Research Laboratory contributes to this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

Electrodialysis has long been used to desalt brackish water. This report describes a pilot scale evaluation of this process for the partial demineralization of wastewater.

ABSTRACT

Demineralization of carbon-treated secondary effluent by a 45.5 lpm (12 gpm) Ionics electrodialysis pilot plant was investigated at the Pomona Advanced Wastewater Treatment Research Facility, Pomona, California.

Slime formation (organic fouling) on the membranes and spacers of the electrodialysis stack during continuous operation significantly decreased the effectiveness of the electrodialysis process to demineralize municipal wastewater. Other forms of stack fouling such as membrane scale were not as serious a problem as organic fouling. An enzyme-detergent (Biz, manufactured by Proctor and Gamble) cleaning technique was developed to minimize organic fouling and thus maintain steady state demineralization conditions. If the total COD of the feedwater was maintained at or below 10 mg/l, a weekly enzyme-detergent flush maintained the total dissolved solids (TDS) removal in the design range of 30-35 percent.

A cost estimate for a 10 MGD single stage electrodialysis plant based on the operating results obtained at Pomona was made. The estimated cost of 19.4¢ per 1,000 gallons was based on the use of carbon-treated secondary effluent with an average TDS concentration of 540 mg/l and a total COD of 10 mg/l or less to produce a product water with 30-35 percent reduction in TDS.

This report was submitted by the County Sanitation Districts of Los Angeles County in fulfillment of Contract 14-12-150, under the partial sponsorship of the Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency. Work was completed as of December 1970.

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The advice and suggestions given by Dr. John Arnold of Ionics, Incs. during the course of study were important contributions to the success of the study.

Helpful review and discussion of the project progress was provided throughout the duration of the investigation by Mr. Charles W. Carry, Assistant Department Head, Technical Services Department, County Sanitation Districts of Los Angeles County.

SECTION 1

CONCLUSIONS

1. Stack fouling due to slime was evidenced whenever an increase in stack pressure was accompanied by a decrease in stack current (amperage) or demineralization.

2. An enzyme-detergent (Biz) was successful in removing most of the slime on the membranes, however, heavy slime formation in the stack, viz, stringy slime found on spacer webbings, was not removed.

3. Scale formation was effectively removed by an acid solution.

4. The degree of organic fouling dictated the frequency and length of the enzyme-detergent portion of the flush cycle (e.g. 30 or 60 minutes). However, see (2) above.

5. An acid solution rinse was required after the enzyme-detergent flush portion of the cycle to remove the detergent and restore the stack amerage.

6. No strong evidence was obtained to demonstrate that a 60 minute rather than a 30 minute acid rinse was more effective.

7. No strong evidence was obtained to demonstrate air-water back-flushing of the dilute compartments was effective for other than removing loose scale, sand, and carbon particles if present in the stack.

8. The quality control tests did not indicate any significant changes in exchange capacities for the cation membranes after 16,136 hours of operation. A 30 percent reduction of the exchange capacity of the anion membranes was noted during the same period of operation. There was no evidence of accelerated membrane deterioration as a result of enzyme-detergent cleaning.

9. To minimize cleaning cost, realize a 30-35 percent conductivity removal, and experience continuous steady-state operation, a weekly enzyme-detergent flush, and stack hand-cleaning and inspection every two-months is necessary with an influent total COD level of about 10 mg/l.

10. A bench-scale current reversal ED unit showed that polarity reversal had no significant effect in retarding slime formation.

11. The estimated cost to produce a product water with 30 to 35 percent TDS reduction in a 10 MGD single stage electrodialysis plant is about 19.4¢ per 1,000 gallons of product water, exclusive of the costs of carbon adsorption pretreatment and brine disposal.

SECTION II

RECOMMENDATIONS

The results of this study indicated that the major problem associated with the electrodialysis process for wastewater demineralization was the formation of scale and slime on the membranes. Although these membrane fouling substances can be effectively removed by regular enzyme-detergent and acid flushing as demonstrated in this study, this membrane cleaning technique may not be the most cost-effective way of operating the electrodialysis plant for wastewater demineralization. Therefore, some other means of preventing the formation of scale and slime on the process membranes require further investigation to optimize the process operation and improve the process cost effectiveness. This may require the removal of calcium to prevent scale formation, and the use of bactericidel techniques to prevent slime growth in the membrane stack.

SECTION III

INTRODUCTION

Electrodialysis is a process used to demineralize, desalt, or deionize water by transporting ions in a direct current (D.C.) electric field through alternating cation and anion membranes. The process was initially used to desalt brackish water.

Technically, electrodialysis should be effective in partial demineralization of municipal wastewater to remove the approximately 300 mg/l total dissolved solids (TDS) added to potable water as a result of domestic usage. Because municipal wastewater (Pomona TDS approximately 540 mg/l) has a lower mineral content than brackish water (TDS approximately 1000 - 10,000 mg/l), the operational cost should be less; however, wastewater contains organic contaminants which adversely affect the operation and performance of the electrodialysis process.

The electrodialysis process (Figure 1) utilizes cation and anion permeable membranes, arranged in an alternating pattern, and placed in the path of an electric current. The "stack" consists of a series of of cell-pairs with each cell-pair consisting of an anion membrane, a spacer, and a cation membrane. The membranes are thin sheets of ion exchange material (0.102 to 1.016 mm thick) containing active ionic groups and a substantial amount of water by weight when in use to enable the active ionic groups to function. The membranes are composed of an inert cross-linked, plastic polymer to which ionizable radicals such as sulfonic acids or amines are attached by a chemical bond. The entire structure contains 15 to 40 percent by weight of water distributed in millions of very fine capillary pores which honeycomb the structure. Membrane pore sizes are of the order of 10 to 100 Angstroms. The fineness of its passages makes the ion transfer membrane virtually impermeable to water at normal pressures.

The anion membranes, which contain ionic amine groups with a fixed positive charge, are capable of repelling other positive ions (cations). The cation membranes, which contain ionic sulfonic acid groups with a fixed negative charge, are capable of repelling other negative ions (anions). The oppositely charged ions are allowed to enter into the fine capillary pores of the membrane and travel through the membrane under the influence of a D.C. electric field, while the identically charged ions are repelled and cannot pass through the membrane. By

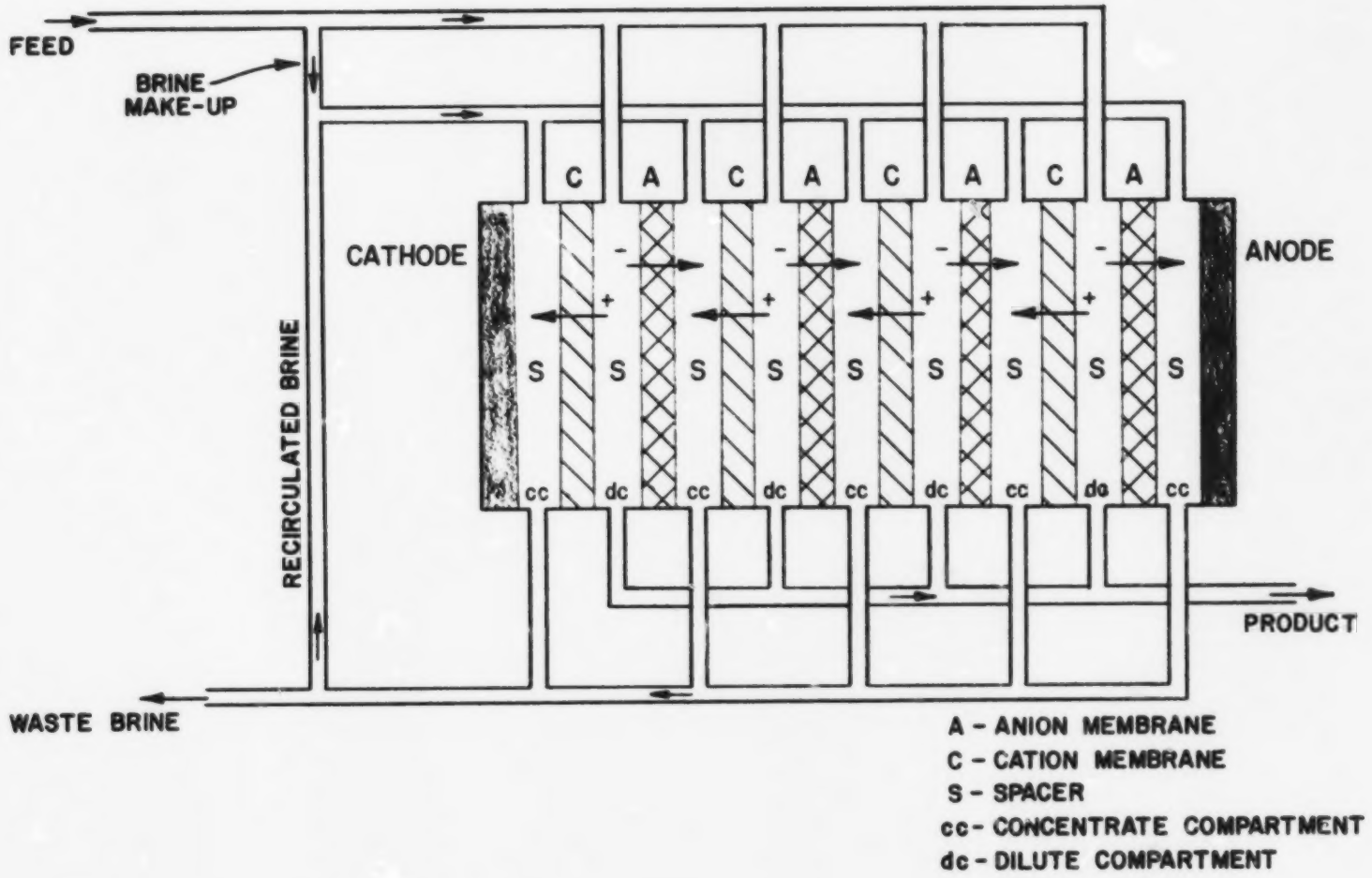

FIGURE I : THE ELECTRODIALYSIS SYSTEM

alternating anion and cation membrane a series of diluted and concentrated compartments are established. The spacers are made of a plastic material and provide a path for the water to travel across the face of each membrane in both dilute and concentrating compartments.

The stack may be regarded as one electrolytic cell, and the standard electrochemical principles apply. The direct current traverses every compartment perpendicular to the membranes between the anode and the cathode. Design and operation of the electrodialysis system depends upon utilization of appropriate membrane properties combined with application of Ohm's and Faraday's Laws. The movement of ions in solutions or through membranes is governed by Faraday's Law and the voltage requirement for an electric membrane system is governed by Ohm's Law.

The specific objectives of this electrodialysis pilot plant study were (1) to investigate the feasibility of wastewater demineralization by the electrodialysis process; (2) to investigate the membrane fouling problems and their control methods; (3) to develop the optimum operating conditions; (4) to demonstrate the reliability of the process performance; and (5) to produce a realistic process cost estimate based on the pilot plant operation experience.

The pilot plant study was conducted with the carbon-treated secondary effluent of the Pomona activated sludge plant from July 1968 to December 1970.

SECTION IV

PILOT PLANT DESCRIPTION

The electrodialysis pilot plant was designed and constructed by Ionics Inc. and employed a single-stage with 65 cell-pairs that was capable of removing about 40 percent of the influent total dissolved solids. The membranes were of the standard brackish water demineralization type and were 45.7 cm x 50.8 cm (18" x 20") with an effective area of 1460 sq. cm. Spacers for the stack were the tortuous path type, 0.102 cm (0.040") thick, which also served as perimeter gaskets. The unit received 45.4 lpm (12 gpm) of carbon-treated secondary effluent and produced 39.7 lpm (10.4 gpm) of product water and 5.7 lpm (1.5 gpm) waste brine (88 percent water recovery). The flow rate through a cell-pair was 10 ml/sec with a residence time of about 15 seconds, while the flow rate through each of the electrode (anode and cathode) compartments was maintained at 18 ml/sec. The brine stream leaving the concentrate compartments was partially recirculated with feed water back into the stack. This method of operation kept the flow rate through the concentrate compartments approximately the same as through the dilute compartments. This resulted in nearly equal pressure on both sides of each membrane and prevented membrane and spacer distortion.

Sulfuric acid was injected into the brine recirculation and cathode streams with diaphragm pumps to prevent scaling problems. A pH control system was used to control brine stream pH between 3.5 and 4.5. Cathode stream pH was held at about 1.5. Totalizing flow meters were provided for the feed and product streams.

Direct current for the stack was provided by silicon cell rectification of a 3 phase, 440 volt source. The electrode system consisted of a stainless steel cathode and a platinized columbium anode.

A 20 cell-pair stack and a current reversal unit were also used for a short period of time to determine the effects of enzyeme-detergent flushing and polarity reversal in retarding slime formation on the membranes.

SECTION V

MEMBRANE CLEANING OPERATIONS

From the beginning of the electrodialysis pilot plant operation on the carbon-treated secondary effluent, membrane fouling problems constantly interfered with the system performance. The fouling was caused by scale and slime formation on the membranes. This in turn caused the operating stack current to decrease from its initial setting of 4 amps to the range of 2 to 3 amps, and the stack pressure to increase from 2.1 kg/sq cm (30.5 psig) to as high as 3.4 kg/sq cm (49.5 psig) within a few days of on-stream operation. Therefore, a great deal of research effort was devoted to the development of membrane cleaning techniques.

A 20 cell-pair experimental unit furnished by Ionics, Inc. was operated at the Pomona Research Facility to simulate the operation conditions of the 65 cell-pair pilot plant, namely flow rate of 10 ml/sec per cell-pair and current density of approximately 3 ma/sq cm. The 20 cell-pair stack was allowed to foul and attempts were made to clean the membranes in-place using the Biz enzyme-detergent, which had shown promising effectiveness in cleaning the reverse osmosis membranes used in the concurrent reverse osmosis pilot plant studies. The use of Biz enzyme-detergent for cleaning the 20 cell-pair stack at Pomona and also some other compatability tests performed by Ionics laboratory did not show any detrimental effects on the membranes. Therefore, the enzyme-detergent cleaning technique was applied to the 65 cell-pair pilot plant.

The enzyme-detergent cleaning solution was prepared by dissolving 1.5 kg of Biz enzyme-detergent in 60 liters of warm tapwater (about 40^{o}C). The flushing procedure was as follows:

(1) Recirculating the Biz enzyme-detergent solution 30 to 60 minutes through the membrane stack;

(2) Flushing the enzyme-detergent solution out of the stack with tapwater for 30 to 60 minutes;

(3) Rinsing the stack with sulfuric acid for 30 to 60 minutes at pH of 2.5 to 3.0; and

(4) Returning the unit to normal operations.

Throughout the flushing cycle, equal flow through the dilute and concentrate compartments was maintained to prevent excessive pressure on one side of the membrane which could cause membrane distortion. The stack current was off during all flushing periods.

To determine if membrane fouling was enhanced by the DC current electrical attraction of the charged organic materials, the 20 cell-pair experimental unit was operated with the rectifier off for a two week period. The rectifier was turned on for 30 minutes once a day to allow an amperage reading. The results of this special study are shown in Figure 2. As indicated in this figure, there was very little difference in the amperage decline rate with or without the operation of the rectifier. Therefore, the DC current is not a significant factor in causing membrane fouling in the electrodialysis process for wastewater demineralization.

Ionics, Inc. also furnished a two-stage electrical and a three-stage hydraulic bench-scale current reversal unit for the purpose of evaluating the effect of current reversal on slime fouling trends. The unit was operated under the similar flow rate and current density as the 65 cell-pair pilot plant. The results of operating the current reversal unit showed that polarity reversal had no effect in retarding slime formation. Membrane sliming occurred even though the electrode polarity was reversed every 15 minutes. This finding supports the finding of no change between rectifier on and off operation as discussed above. However, the reversal of electrode polarity did provide a means for controlling scale that did not require the use of acid in the concentrating compartments.

Organic fouling of membranes constituted the primary and most significant disadvantage to the electrodialysis process in demineralizing wastewater. Chemical characterization of the slime material scraped from the electrodialysis membranes at Pomona indicated a formula of $C_7H_{12}O_3N$, which is slightly different from the reported $C_5H_9O_3N$ for the chemical composition of biological slimes in anaerobic treatment systems. Microscopic examinations were also performed on the slimes scraped from the membranes. These examinations always showed bacteria as well as fungi, protozoa, worms, and other debris. In addition, microbiological studies of these slimes showed heavy growth within 24 hours on an anaerobic culture media and medium to heavy growths on aerobic, fungi, and mold culture media.

Removal of these biological slimes required manual cleaning of the membranes and normally entailed the following:

(1) Stack disassembly;

(2) Cleaning of each individual membrane and spacer with a scrub brush or fine steel wool, and a dilute acid solution; and

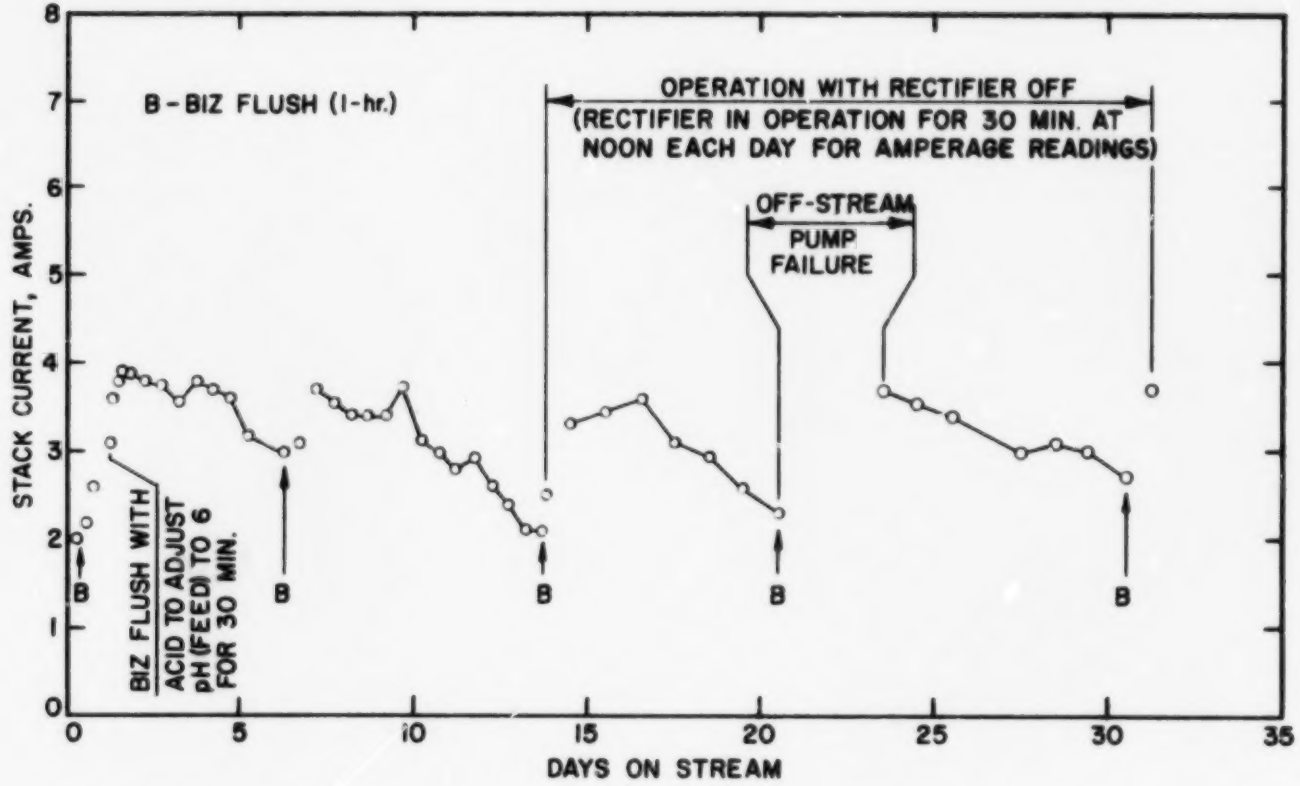

FIGURE 2: THE EFFECT OF DC CURRENT ON MEMBRANE FOULING

(3) Stack reassembly.

Approximately 6 to 8 man-hours were required to accomplish this task on a Mark II 65 cell-pair stack.

To minimize the "out of service" time required to clean the membranes, a program was initiated to evaluate the use of enzyme-detergent flushing procedures. The following five procedures were evaluated for the length of time shown:

(1) Enzyme-detergent flush the unit on an as-required basis when the demineralization level dropped below 25 percent - 273 days;

(2) Enzyme-detergent flush the unit daily - 51 days;

(3) Enzyme-detergent flush the unit every other day - 68 days;

(4) Enzyme-detergent flush the unit weekly - 92 days; and

(5) Enzyme-detergent flush the unit every other week - 72 days.

The unit operation and performance of each of these five cleaning sequences will be discussed individually.

As - Required Enzyme-Detergent Cycle

During this 273 day period the unit was allowed to operate continuously until the demineralization level dropped below 25 percent. At this point, the stack current had decreased from 4 amps to approximately 2 amps and the stack pressure had increased from 2.1 kg/sq cm (30.5 psig) to approximately 3.3 kg/sq cm (48 psig). To remove the organic foulants the stack was flushed with an enzyme-detergent solution according to the procedures described earlier. A total of six enzyme-detergent flushings were applied to the unit during the 273 day cycle.

Poor stack performance, characterized by reduced TDS removal, low stack amperage and high stack pressure, necessitated stack disassembly and inspection 47 days after start-up. The inspection showed:

(1) Slime formation throughout the stack membranes;

(2) One anion membrane was moderately scaled and had to be replaced; and

(3) Slight scaling on all anion membranes at spacer webbings.

Approximately 77 days after start-up, high stack resistance was noted and resulted in reduced current and demineralization performance and dictated stack disassembly, inspection, and hand cleaning. This occurred

despite two enzyme detergent flushings that were conducted a week apart. The reduction in current was not accompanied by high stack pressure, so scaling rather than slime fouling of the membranes was assumed. Stack disassembly showed scaling in the anion membranes in the concentrate compartments. The scale was removed by using a dilute sulfuric acid solution and by lightly rubbing the membranes with steel wool.

In addition to the presence of scale, particles of undissolved light bluish colored enzyme-detergent were detected under spacer webbings. To more effectively remove the foulants and the cleaning agent, the piping was modified to allow by-passing the brine recirculation pump and to provide identical flows through both the dilute and concentrate compartments during the flushing operation.

Eighty-two days after start-up, abrupt stack pressure increased and stack amperage declined with resultant decline in demineralization. This coincided with periods of methanol leakage from the carbon column that supplied water to the electrodialysis unit. Methanol was used in the carbon column during a denitrification study. COD values as high as 50 mg/l were recorded in the carbon effluent feed to the unit. Stack inspection showed a large build-up of slime particularly in the dilute compartments.

The enzyme-detergent was not effective in removing the slime found in the dilute compartments caused by the high feed COD, nor was it effective in removing slime that accumulated during long periods of operation between cleanings. On several occasions shortly after enzyme-detergent flushing, the stack was inspected and the stringy slime formation on the spacer webbings remained. Unit operation under these conditions resulted in a current of 3.2 to 3.5 amps with about a 34 percent conductivity reduction. These conditions ordinarily reflect clean membranes. However, due to the unremoved slime the stack pressure was increased from 2.1 kg/sq cm (30.5 psig) to 3.3 kg/sq cm (48 psig) and the flow decreased from 38 l pm (10 gpm) to 36 l pm (9.6 gpm). To restore normal flow, hand-cleaning of the spacers with a scrub brush was necessary.

Occasional air-water backflushing of the dilute compartments was effective in removing loose scale, sand and carbon particles if present in the stack and thereby helped lengthen the operating time between enzyme-detergent flushings throughout the 273-day study. The air-water backflushing procedure normally required 10 to 20 minutes to complete.

Daily Enzyme-Detergent Cycle

Unit performance for this 51-day study is shown in Figure 3. The influent total and dissolved COD averages were 11.6 mg/l and 7.8 mg/l, respectively. Stack pressures above 2.3 kg/sq cm (34 psig) shown in

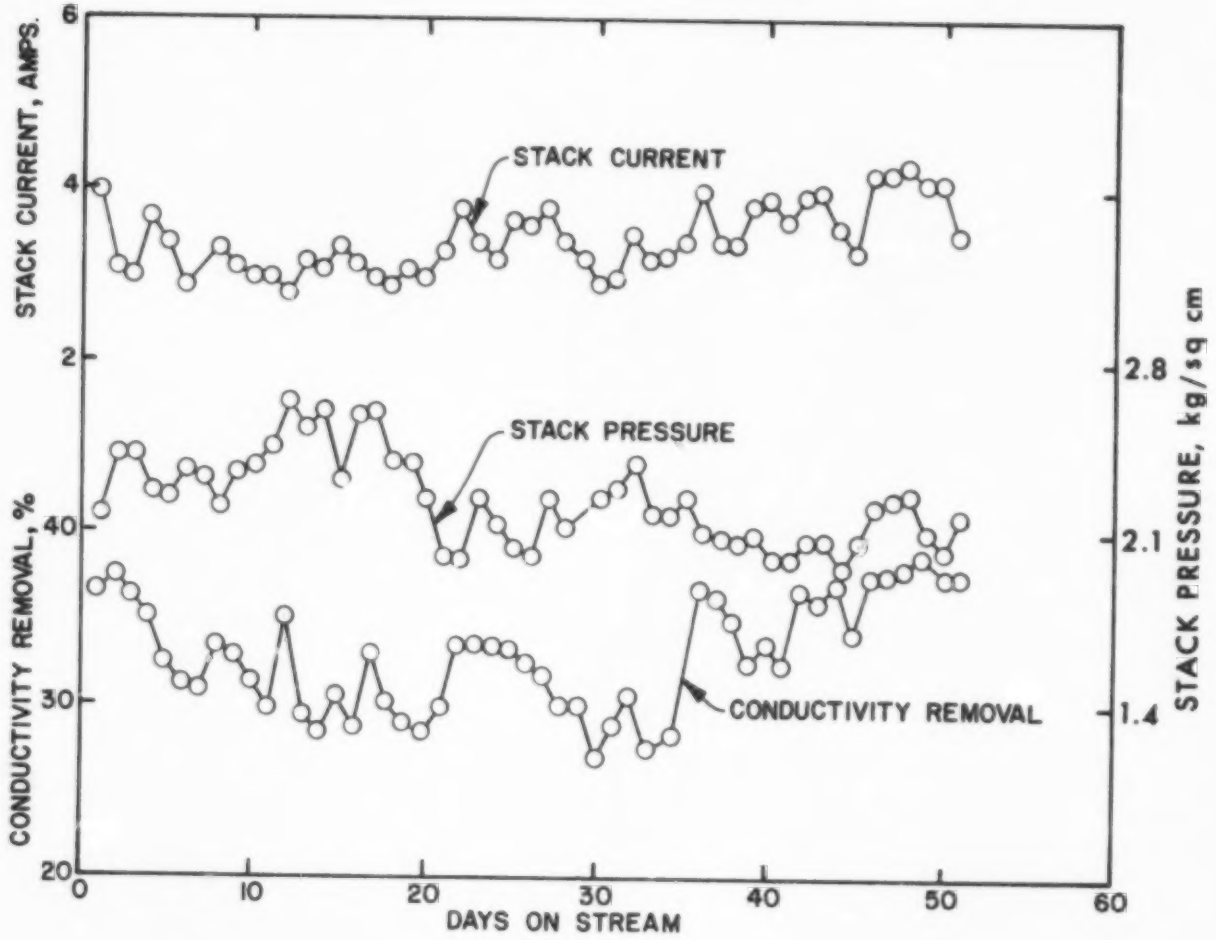

FIGURE 3: DAILY ENZYME - DETERGENT CYCLE

Figure 3 were a result of influent COD concentrations of 15 mg/l to 20 mg/l. The unit operated for 1,087 hours at approximately 90 percent water recovery. The average feed and product conductivities were 869 μmhos/cm and 583 μmhos/cm, respectively, a reduction of 33 percent.

Several flushing methods were investigated during the daily enzyme-detergent flush cycle study. These were:

(1) 30 minutes enzyme-detergent, 30 minutes water and 30 minutes air-water flush;

(2) 30 minutes enzyme-detergent, 30 minutes water and 30 minutes acid solution flush;

(3) 30 minutes enzyme-detergent, 30 minutes water, 30 minutes acid solution and 10 minutes air-water flush;

(4) 60 minutes enzyme-detergent, 60 minutes water, 60 minutes acid solution and 10 air-water flush; and

(5) 30 minutes enzyme-detergent, 30 minutes water and 60 minutes acid solution flush.

The results of employing these various methods of flushing the membranes are identified and shown in Table 1.

It was concluded that a 90 minute flushing period was adequate and that an acid solution rinse was necessary in the enzyme-detergent cycle to insure stack amperage recovery. These results confirmed earlier studies by Ionics that showed a high resistance film, removable by hydrogen ion, adhered to the membrane after soaking in an enzyme-detergent cleaning solution. However, it should be noted that the stack amperage loss without the acid flush was temporary; the amperage readings would usually return to normal the day after the membrane flushing. The four methods that included an acid rinse were all effective in recovering the stack current. There was no strong evidence that: (1) 60 minutes of acid flush was more effective than 30 minutes of acid flush, and (2) air-water flush was effective other than to remove loose scale, sand, and carbon particles if present in the stack. The time (30 or 60 minutes) required in the enzyme-detergent portion of the cycle would be dependent upon the extent of slime formation on the membranes and spacers in the dilute compartments.

Every-Other Day Enzyme-Detergent Cycle

Unit performance for the 68 day study is shown in Figure 4. The total and dissolved feed COD averages were 5.9 mg/l and 5.1 mg/l,

TABLE 1

SUMMARY OF PILOT PLANT OPERATIONS WITH DIFFERENT MODES OF

DAILY ENZYME-DETERGENT FLUSHING PROCEDURES

Mode[1] of Flushing	Testing Period (day)	Average Stack Pressure (psig) (2)		Average Stack Current (amps)	
		Before	After	Before	After
A	10	31.6	29.8	3.2	2.5
B	10	34.8	32.6	2.9	3.1
C	11	31.2	29.7	3.2	3.4
D	10	31.4	29.9	3.2	3.5
E	10	30.5	29.9	3.7	3.9

(1) Mode of Flushing:

A - 30 min. Enzyme-detergent, 30 min. water and 30 min. air-water flush.
B - 30 min. Enzyme-detergent, 30 min. water and 30 min. acid flush.
C - 30 min. Enzyme-detergent, 30 min. water, 30 min. acid and 10 min. air-water flush.
D - 60 min. Enzyme-detergent, 60 min. water, 60 min. acid and 10 min. air-water flush.
E - 30 min. Enzyme-detergent, 30 min. water and 60 min. acid flush.

(2) 1 psig = 0.0703 kg/sq cm

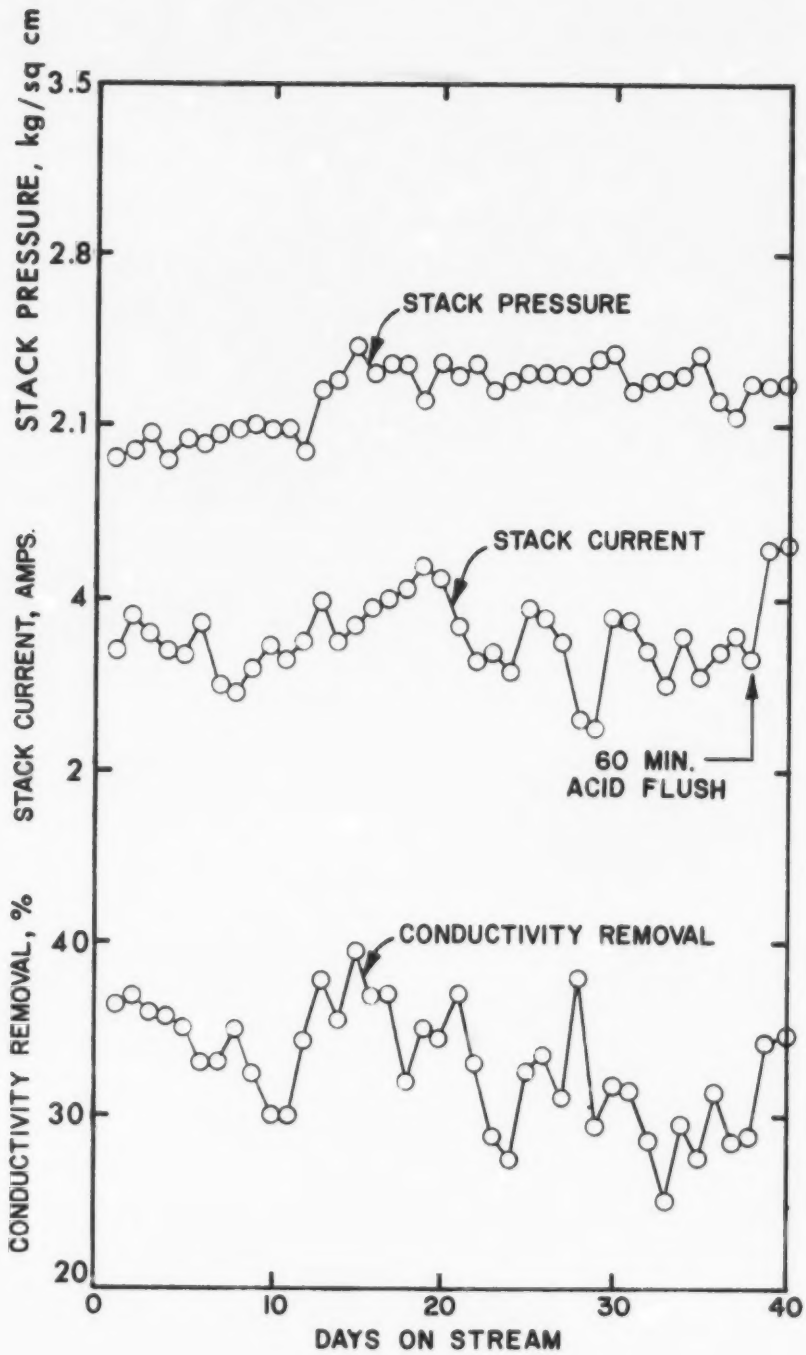

FIGURE 4: EVERY-OTHER-DAY ENZYME-DETERGENT CYCLE

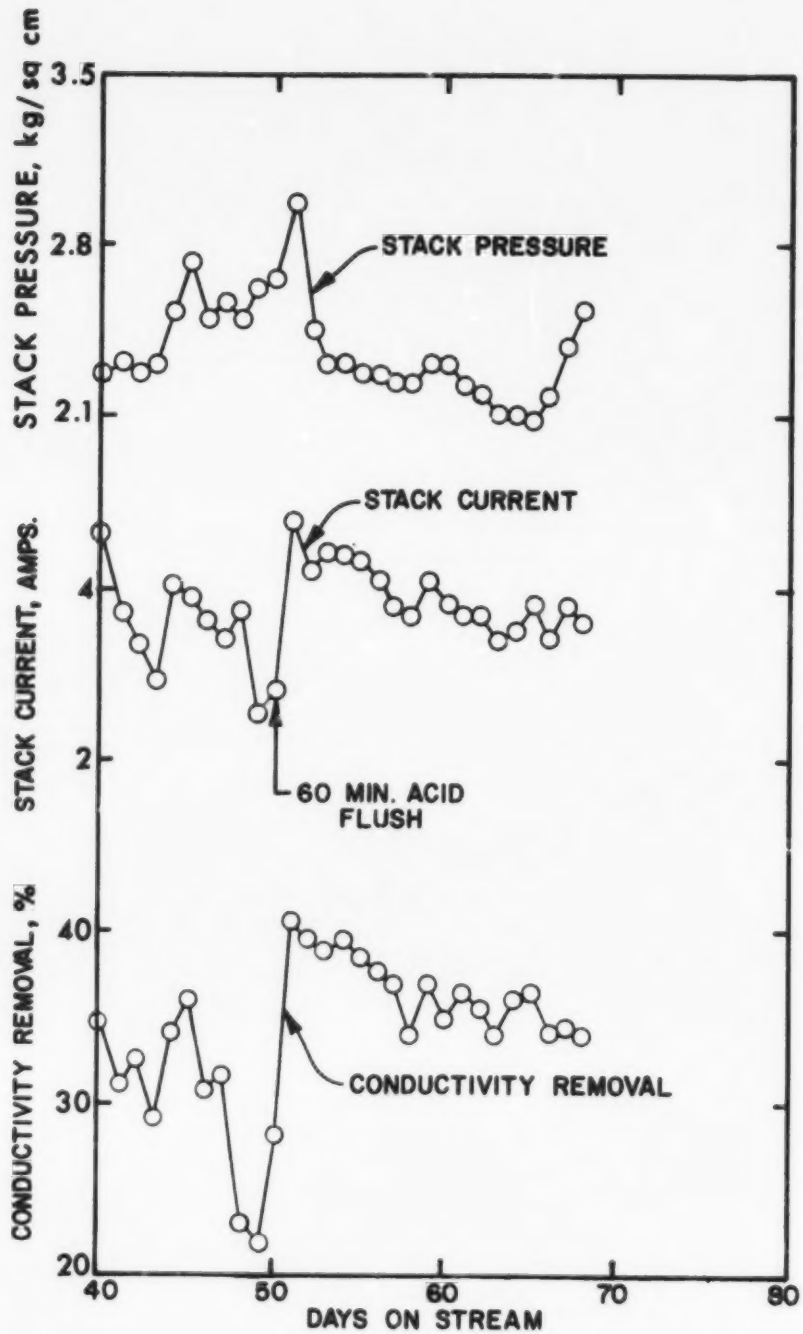

FIGURE 4 : (CONTINUED)

respectively. The average feed and product conductivities for the study were 982 and 658 μmhos/cm, respectively, a reduction of 33 percent. A routine stack inspection was conducted at 30 days into the study to see the effect of the flushing procedure upon the membranes. The inspection did not reveal any excessive slime or scale build-up. The stack was exceptionally clean with only a few isolated carbon and sand particles. This could be partially attributed to the additional 10 minute air-water flush employed between enzyme-detergent flushings. However, this mode of membrane cleaning was not able to restore the stack current to the expected level. On 38th day of the study, an hour of acid flush was applied in addition to the routine enzyme-detergent flushing. This additional acid flush was effective in restoring the stack current from 3.3 amps to 4.7 amps. The conductivity removal through the unit was also improved from 28 percent to 34.5 percent as a result of the acid flush.

Significant changes in unit performance occurred on the 48th and 49th days, as the conductivity removal declined to less than 25 percent. Enzyme-detergent flushing did not restore the performance to the expected level. An hour of acid flush was able to restore the stack current but not the stack pressure. The stack was finally inspected on the 51st day to determine the cause of the high stack pressure. The inspection showed that the membranes and spacers were exceptionally clean with very little slime and scale formation. However, there was a heavy accumulation of calcium carbonate on the cathode plate and in the cathode compartment. The calcium carbonate deposits were removed by a dilute acid solution wash and rubbing with fine steel wool. The membranes and spacers were rinsed in tapwater before the stack was reassembled and put back on stream with normal stack pressure and current readings of 2.3 kg/sq cm (33.5 psig) and 4.2 amps, respectively.

The excessive deposits of calcium carbonate occurred on two separate occasions during a 7 day period because no acid was being added into the cathode compartment to prevent scaling or calcium carbonate build-up. Each occasion lasted for 12 hours and was caused by air-locking of the acid pump.

The stack was inspected at the end of the study to determine the cause of the sudden stack pressure increase as shown in Figure 4. Just prior to disassembling the stack it was probed. Stack probing involved indirectly determining the resistance of the stack using volt meter. The probing was started at the top of the stack and the voltage for every inch of the entire stack was taken. A high voltage reading, corresponding to a high internal resistance, as compared to the other readings of any one inch segment of the stack would indicate the location of a possible problem area. The results of the stack probing did not locate any trouble spot which could be responsible for the stack pressure increase. Consequently, the stack was disassembled to inspect the condition of the membranes. Very little slime and

scale formation on the membranes were noticed during the inspection. The cathode compartment was found free of calcium carbonate deposits that were noted previously. The reason for the pressure increase toward the end of the study was not readily apparent.

Weekly Enzyme-Detergent Cycle

Performance for this 92 day study is shown in Figure 5. The unit operated for 2,019 hours at approximately 91 percent water recovery. The average feed and product conductivities were 804 and 555 μmhos/cm, respectively, a reduction of 31 percent. The influent total and dissolved COD averages were 9.1 and 6.9 mg/l, respectively.

At the start of the study, the stack was disassembled and the membranes and spacers were rinsed in tapwater to remove small amounts of sand, carbon particles, and slime in the dilute and concentrate compartments. Ten days later, because of high stack pressure and poor performance, the stack was inspected and hand-cleaned to remove the slime and small amounts of scale under spacer webbings. The stack was not disassembled or hand-cleaned again until the end of the study, at which time a significant amount of slime was present on the membranes and spacers in the dilute compartments.

It was found that the weekly enzyme-detergent cleaning schedule was not able to maintain a steady stack current between the cleaning cycles. The conductivity removal was reduced as a result of the decline of the stack current. Therefore, a 30 minute acid rinse with or without a 10 minute air water flushing, depending on the extent of the build-up of the stack pressure, was employed between the enzyme-detergent cleaning cycles to maintain a rather steady unit performance. As indicated in Figure 5, the conductivity removal showed a definite decline trend during the last 25 days of the study. This could be attributed to the inadequate membrane cleaning procedures. The stack inspection at the completion of the study did show a significant amount of slime on the membranes in the dilute compartments.

Every Other Week Enzyme-Detergent Cycle

The unit was operated with this cleaning schedule for a total of 72 days. The various performance data are shown in Figure 6. The overall average of the water recovery during this study period was approximately 91 percent. The average feed and product conductivities were 806 and 583 μmhos/cm, respectively, a reduction of 27.6 percent. The influent total and dissolved COD averaged 7.1 and 5.4 mg/l, respectively.

The stack was hand-cleaned prior to initiating the 72 day study. Due to declining stack performance, the stack was inspected after the first

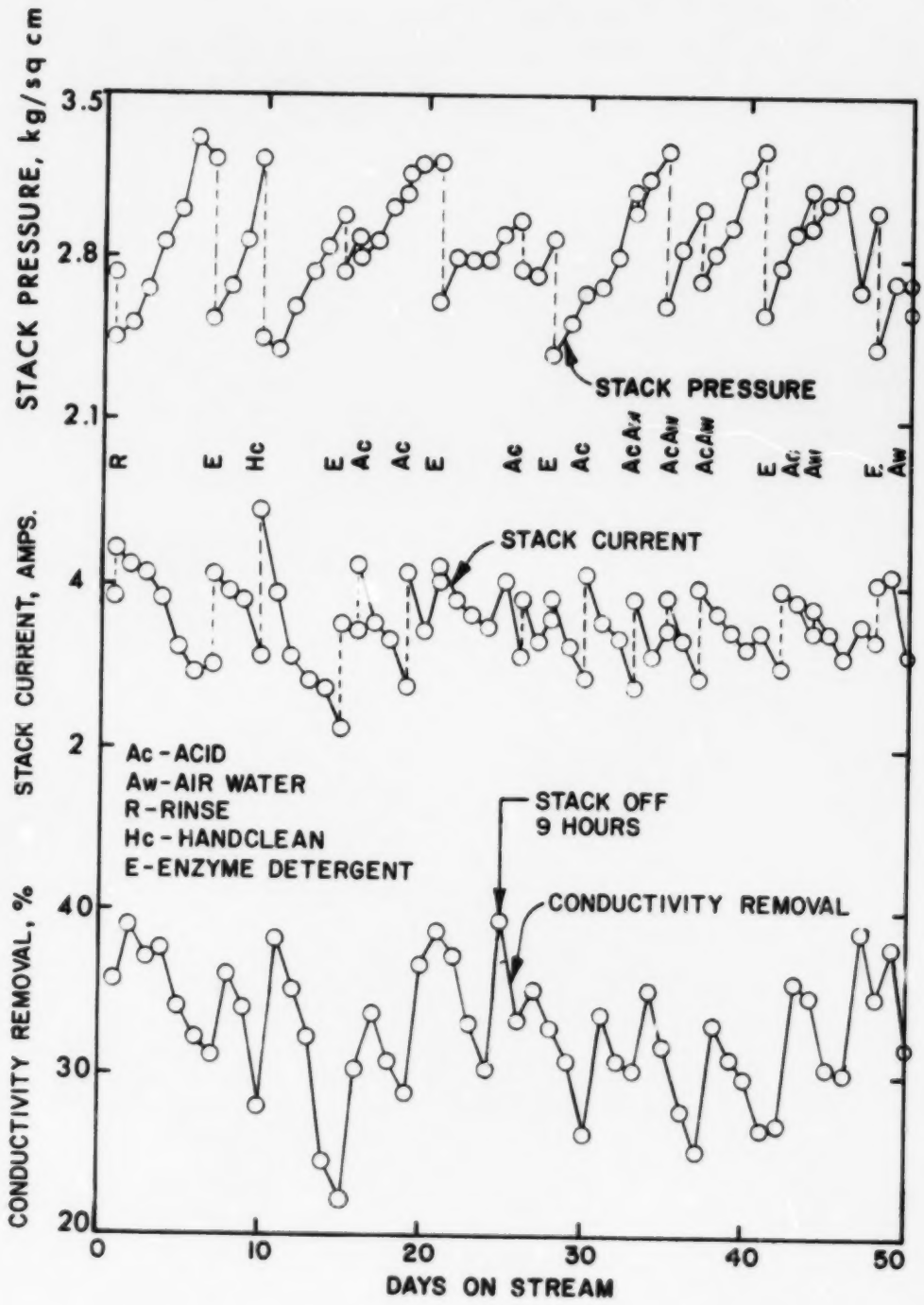

FIGURE 5: WEEKLY ENZYME-DETERGENT CYCLE

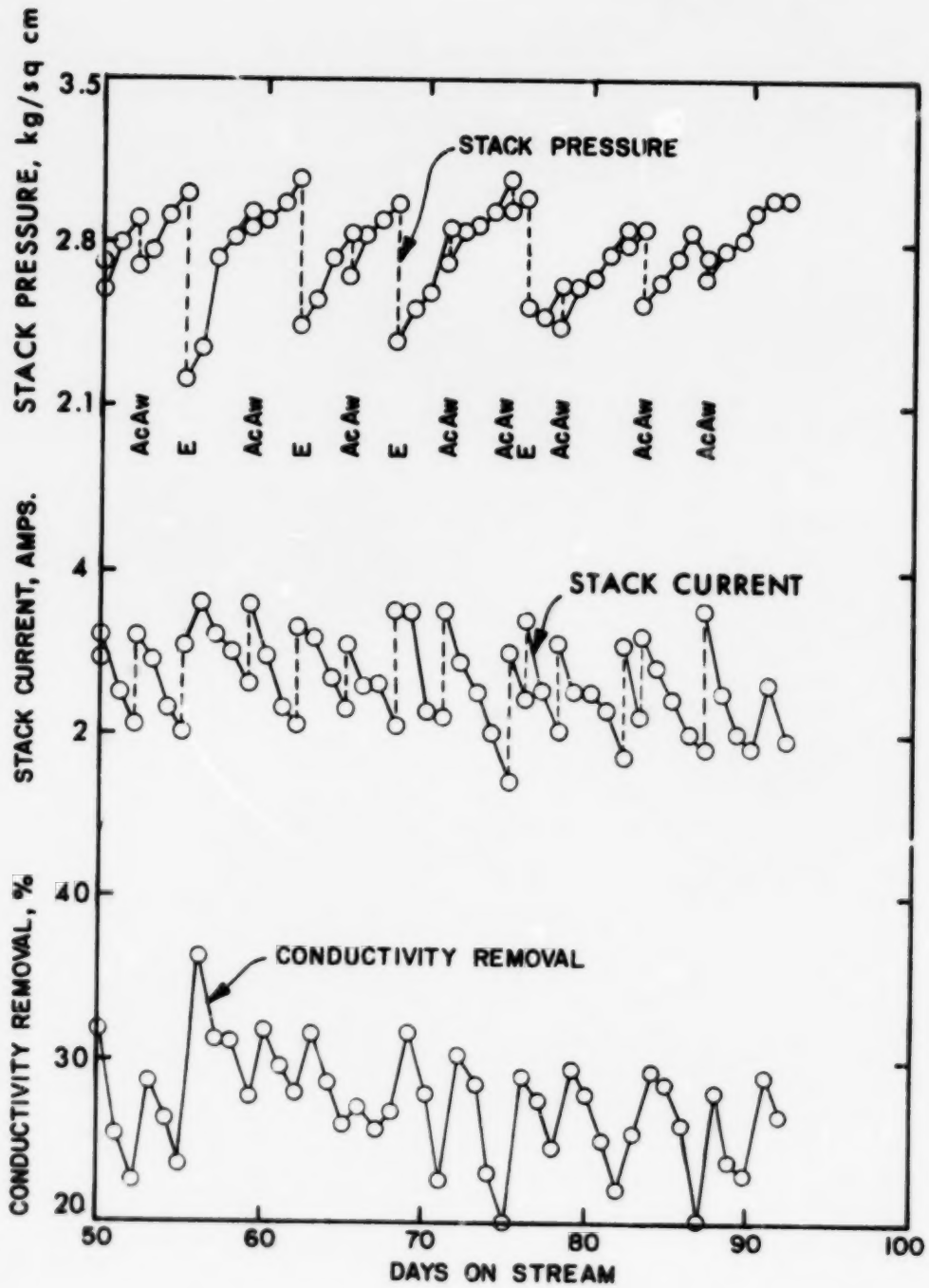

FIGURE 5: (CONTINUED)

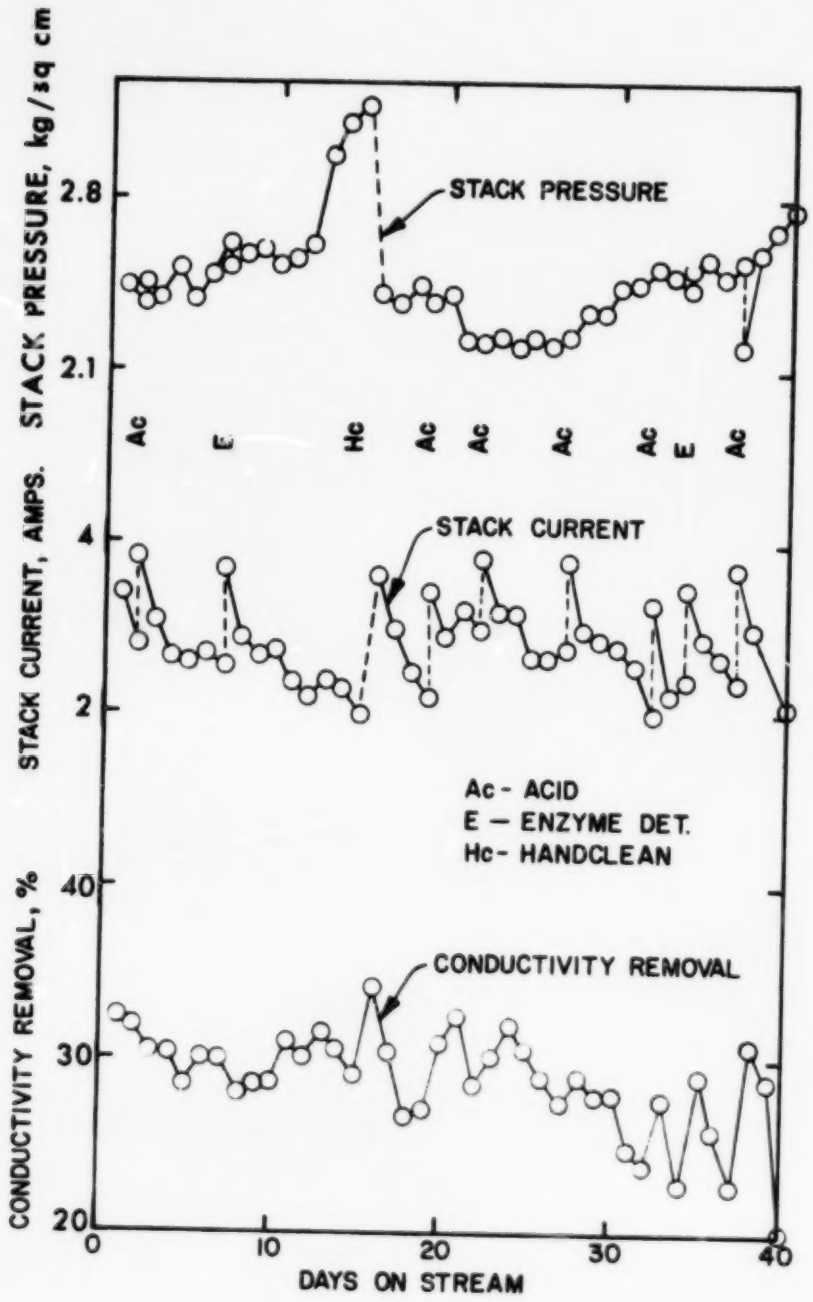

FIGURE 6: EVERY-OTHER-WEEK ENZYME-DETERGENT CYCLE

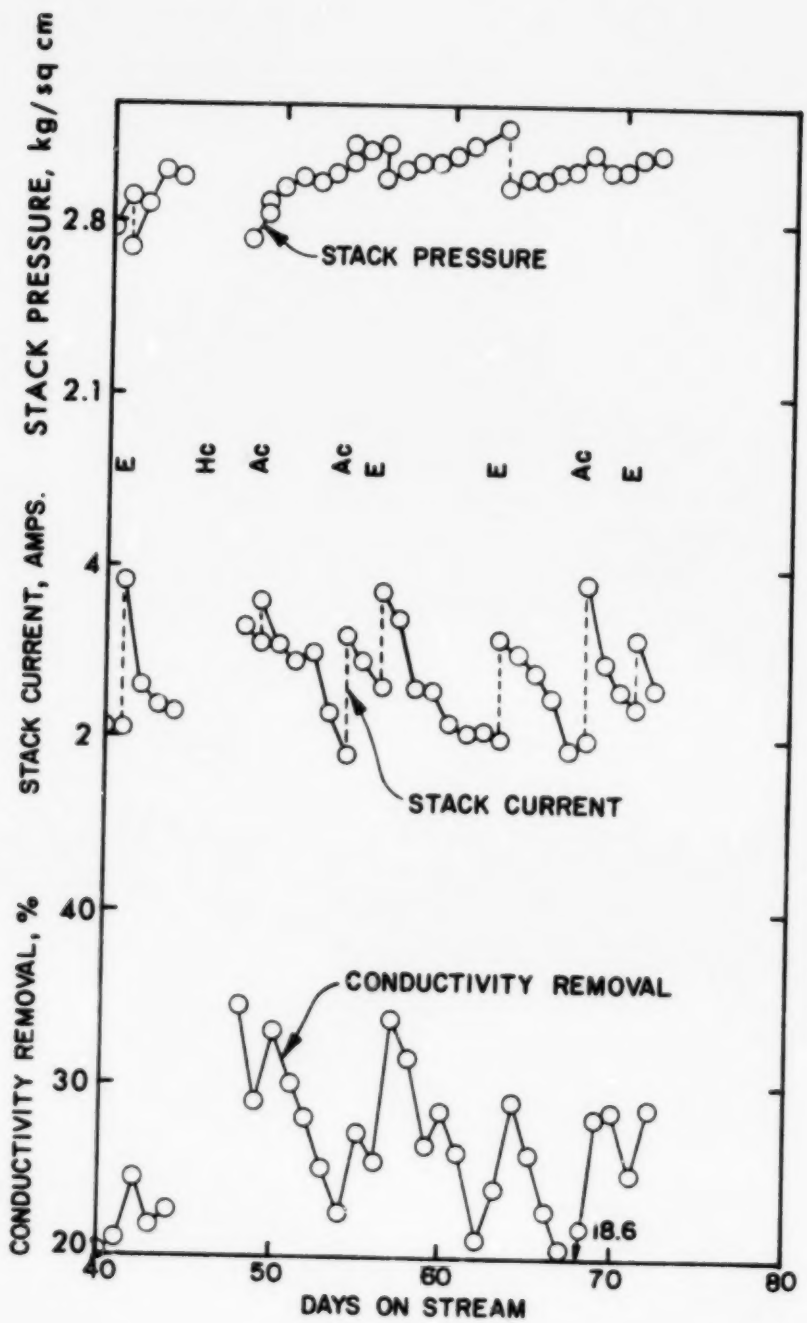

FIGURE 6: (CONTINUED)

15 days of operation and showed the presence of large quantities of brownish colored slime (previous slime color was gray) on the membranes and spacers in the dilute compartments. Scaling was also evident on some of the membranes. Slime was also found on the glass of the feed and brine make-up rotometers so they were dismantled and cleaned. The declining performance during the first 15 days of operation could be due to the deteriorated influent quality. The average COD of the feed for a seven-day period prior to the stack inspection on the 15th day was about 13.1 mg/l. The stack was hand-cleaned and it was returned to service receiving influent water with a COD of less than 10 mg/l.

On the 44th day, the stack was again inspected due to an overall decline in unit performance. The enzyme-detergent and acid flush did not maintain stack performance. Stack inspection showed very little slime and scale build-up on the membranes and spacers; however, one of the spacers was found to be placed incorrectly in the stack. The mistake had occurred during the hand-cleaning on the 15th day. The anion membrane associated with the misplaced spacer was completely covered with scale and showed evidence of deterioration. Corrective action was taken, and the unit was back on stream four days later. In spite of cleaning the stack and replacing the anion membrane, further operation with this mode of membrane cleaning schedule continued to show a definite decline in the unit performance.

The overall unit performance, as reflected by the conductivity removal, under the above five different modes of membrane cleaning procedures is summarized in Table 2 . As expected, the enzyme-detergent cleaning of the stack at more frequent intervals resulted in cleaner membranes, hence higher conductivity removals. However, when the expensive cost for high frequency membrane cleaning is considered together with the slight gain in the conductivity removal as indicated in Table 2 , it is better to use a less frequent cleaning schedule for the unit operation. A weekly enzyme-detergent cleaning cycle will be employed as the basis for process cost estimate in this report.

TABLE 2

SUMMARY OF CONDUCTIVITY REDUCTION

Frequency of Enzyme-Detergent Cleaning	Period of Study (days)	Average Conductivity Reduction (%)
As-Required	273	29
Daily	51	33
Every-other-day	68	33
Weekly	92	31
Every-other-week	72	28

SECTION VI

PERFORMANCE DATA

The average concentrations of the major ions found in the feed and product waters for a six month period, April 1970 through September 1970, are shown in Table 3. The ion removal and ion selectivity, which is defined as the ratio of the percentage removal of a given ion to the percentage removal of all ions, are also shown in Table 3.

As indicated in Table 3, the bivalent cations seemed to be more efficiently removed than the monovalent cations. However, the monovalent anions demonstrated higher removal than the bivalent anions.

The ion selectivity as defined above can be affected by many parameters. These may include pH, influent constituents, membrane structure, polarization, membrane fouling, etc. The selectivity for sulfate ion was found to decrease significantly with an increase in membrane fouling. The phosphate ion selectivity was also found to behave similarly as sulfate ion but not as significantly. Generally, as expected, the ion removal by the electrodialysis process was not specific.

A typical set of the heavy metal concentrations in various process streams is shown in Table 4. The heavy metal concentrations in the process feed water were too low to provide any conclusive evaluation of the process capability in heavy metal removal.

As shown in Table 5, the electrodialysis process was able to remove some of the refractory organic substances remaining in the carbon-treated secondary effluent, which was used as the feed water for the electrodialysis pilot plant operation. The organics removal could be attributed to the biological activity in the form of slime formation in the membrane stack.

TABLE 3

MAJOR ION REMOVAL AND SELECTIVITY DATA

(April 1970 through September 1970)

Ions	Feed mg/l	Product mg/l	% Removal	Selectivity
Na^+	118.5	92.9	22	0.691
K^+	11.8	8.6	27	0.867
NH_4^+	12.1	8.5	30	0.953
Ca^{++}	62.6	35.5	43	1.384
Mg^{++}	12.7	7.2	43	1.385
Cl^-	109.9	61.6	44	1.406
NO_3^-	12.4	7.5	39	1.256
$SO_4^=$	71.1	53.3	25	0.812
$H_2PO_4^-$	14.6	11.7	18	0.591
$HPO_4^=$	19.1	14.0	27	0.854
HCO_3^-	268	200	25	0.814

TABLE 4

TYPICAL HEAVY METAL CONCENTRATION DATA

(May 6, 1970)

Heavy Metal	Feed Water	Product Water	Waste Brine
Aluminum, mg/l Al	0.00	0.00	0.07
Arsenic, mg/l As	0.00	0.00	0.00
Boron, mg/l B	0.82	0.73	1.10
Cadmium, mg/l Cd	0.006	0.006	0.008
Chromium, mg/l Cr	0.01	0.01	0.01
Copper, mg/l Cu	0.02	0.02	0.02
Iron, mg/l Fe	0.00	0.00	0.00
Lead, mg/l Pb	0.001	0.001	0.001
Lithium, mg/l Li	0.03	0.02	0.03
Manganese, mg/l Mn	0.00	0.00	0.00
Nickel, mg/l Ni	0.26	0.16	0.62
Zinc, mg/l Zn	0.06	0.02	0.20

TABLE 5

REMOVAL OF COD[1], TOC[2], TDS[3], AND TURBIDITY

(April 1970 through September 1970)

Parameter	Feed Water	Product Water	% Removal
Total COD, mg/l	7.9	6.3	20
Dissolved COD, mg/l	6.2	5.2	16
Total TOC, mg/l	2.2	1.6	27
Dissolved TOC, mg/l	1.9	1.4	26
TDS, mg/l	536	361	33
Turbidity, JTU	1.0	0.6	40

(1) COD = Chemical oxygen demand.

(2) TOC = Total organic carbon.

(3) TDS = Total dissolved solids.

SECTION VII

MEMBRANE LIFE

As described earlier, membrane fouling was the major problem encountered with the operation of the electrodialysis process for wastewater demineralization. However, the fouling was not permanent, since cleaning the membranes and spacers resulted in restoration of the design performance conditions. Occasionally, the membranes with extensive scaling had to be replaced because the scale would penetrate and could permanently damage the membranes. Also, the anionic detergents present in the wastewater are known to damage anion membranes permanently; however, the carbon adsorption pretreatment had reduced the concentration of the methylene blue active substances (MBAS) to an insignificant level of 0.05 mg/l or less.

Membrane life data as measured by Ionics quality control tests are shown in Tables 6, 7 and 8. The tests were performed on membranes that had been in operation for 1,320, 4,100, 9,930, and 16,136 hours in the 65 cell-pair stack and on membranes that had been utilized for 600 hours of operation in the 20 cell-pair stack. The quality control tests did not indicate any significant changes in exchange capacities for anion membranes were reduced approximately 30 percent on the tested membranes after one year of on-stream operation. The resistances of the anion membranes were also found to increase substantially in the membrane control tests. However, deterioration of the anion membrane was not well demonstrated in the pilot plant operation since the average conductivity removal during the 2.5 years of pilot plant study always ranged between 28 to 33 percent, depending on the type of membrane cleaning procedure being employed.

Based on the membrane performance during this study and adequate maintenance and competent operating personnel, anticipated membrane life will be 5 years, i.e., 20 percent replacement every year. This figure was used to prepare the process cost estimate.

TABLE 6

20 CELL- PAIR STACK MEMBRANE QUALITY CONTROL TESTS

Membrane	cation		cation	
Batch No.	773C		811A	
Time (hrs)	0	600 (1)	0	600 (1)
Leak Test	-	2 pin holes		tight
Mullen Burst (psi)	95	111	126	122
Resistance (ohm-cm^2)	11.4	12.2	12.5	17.6
Thickness (cm)	0.053	0.052	0.056	0.049
Water Content (%)	42.7	42.8	48.8	48.4
Strong Capacity (meq/dgr)	3.20	2.80	1.42	1.40
Weak Capacity (meq/dgr)	-	-	-	0.75

(1) Including 2 enzyme-detergent cleanings.

TABLE 7

65 CELL-PAIR STACK CATION MEMBRANE QUALITY CONTROL TESTS

Membrane	cation		cation		cation		cation	
Batch No.	673A		673A		673A		671B	
Time (hrs)	0	1,320	0	4,100	0	9,930(1)	0	16,136(2)
Leak Test	-	tight	-	tight	-	-		(3)
Mullen Burst (psi)	133	127	133	136	133	135	126	135
Resistance (ohm-cm^2)	12.3	14.6	12.3	13.4	12.3	15.8	15.6	12.5
Thickness (cm)	0.054	0.056	0.054	0.054	0.054	0.062	0.058	0.054
Water Content (%)	46.4	47.6	46.4	47.8	46.4	48.7	48.4	48.6
Strong Capacity (meq/dgr)	2.61	2.32	2.61	2.60	2.56	2.46	2.66	2.73
Weak Capacity (meq/dgr)	-	-	-	-	-	-	-	-

(1) Including 30 enzyme-detergent cleanings.
(2) Including 115 enzyme-detergent cleanings.
(3) Leaking entire spacer outline.

TABLE 8

65 CELL-PAIR STACK ANION MEMBRANE QUALITY CONTROL TESTS

Membrane	anion		anion		anion		anion	
Batch No.	658A		659C		(1)		(1)	
Time (hrs)	0	1,320	0	4,100	0	9,930(2)	0	16,136(3)
Leak Test	-	tight	-	tight	-	-	-	tight
Mullen Burst (psi)	119	130	119	137	-	130	-	146
Resistance (ohm-cm^2)	12.9	18.3	13.7	16.8	-	25.2	-	20.6
Thickness (cm)	0.058	0.058	0.059	0.054	-	0.058	-	0.058
Water Content (%)	44.2	45.7	44.9	46.6	-	47.3	-	48.9
Strong Capacity (meq/dgr)	1.67	1.49	1.60	1.68	-	1.16	-	1.02
Weak Capacity (meq/dgr)	-	0.73	-	0.69	-	0.44	-	-

(1) No visible batch no. identification, assume original analysis similar to batch no. 658A or 659C for comparison purposes.
(2) Including 30 enzyme-detergent cleanings.
(3) Including 115 enzyme-detergent cleanings.

SECTION VIII

PROCESS COST ESTIMATE

A cost estimate for a 37,850 m^3/day (10 MGD), single stage electrodialysis plant based on the operating results obtained at the Pomona Research Facility is shown in Table 9. More specifically, the cost estimate is based on the following parameters that were developed from the Pomona pilot plant study:

(1) The influent of the electrodialysis plant is a carbon-treated secondary effluent with a total COD level of 10 mg/l or less;

(2) The influent TDS level is approximately 550 mg/l, and a 30 to 35 percent TDS removal is achieved by the single stage electrodialysis plant;

(3) A weekly, enzyme-detergent and acid flush are required for membrane cleaning;

(4) The membrane stack is disassembled once every two months for membrane inspection and maintenance, and

(5) A five-year membrane life is assumed for an electrodialysis process for demineralizing wastewater.

The other factors that were used to determine the costs are included in Table 9. The capital cost of $1,764,000 includes site preparation and 20 percent for contingencies. The cost of the carbon adsorption pretreatment to reduce the secondary effluent total COD from 40 mg/l to 10 mg/l or less is not included in the total process cost estimate. The carbon adsorption pretreatment cost is estimated to be about 9.6 ¢/1000 gallons. The cost of brine disposal is also not included in the process cost estimate. The brine disposal cost may vary substantially from one plant to another depending on the type of brine disposal and the geographical location of plant.

TABLE 9

ELECTRODIALYSIS PROCESS COST ESTIMATE

37,850 m^3/day (10 MGD) PLANT

		¢/1000 gallons
Amortization of Capital		
$1,764,000; 20 years at 6%		4.7
Operation and Maintenance		
Sulfuric Acid ($40/ton)	4.0	
Enzyme-Detergent ($1.2/Kg)	1.2	
Membrane Replacement (5 year life)	4.2	
Maintenance Materials	0.9	
Power ($0.01/kWh)	2.8	
Labor (5 man-days/day)	1.6	
		14.7
	TOTAL	19.4